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A REVIEW OF ATOMIC AND MOLECULAR EXCITATION MECHANISMS IN NONEQUILIBRIUM GASES UP TO 20,000°K

Forrest R. Gilmore, Ernest Bauer and J. William McGowan

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PREFACE

Many problems of interest to the defense community involve heated or excited gases in nonequilibrium conditions. Such problems occur in the fields of hypersonic reentry physics, nuclear weapons effects, fuel combustion and detonation, gas masers and lasers, upper-atmosphere physics, etc. The present review summarizes our knowledge of the atomic and molecular mechanisms that are important in such situations. It should be useful to scientists working in any of the fields mentioned above.

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SUMMARY

This review summarizes present knowledge of the atomic and molecular mechanisms that produce or remove rotationally, vibrationally, and electronically excited species in heated or excited gases. A logical classification scheme for these mechanisms is introduced, and the extent of present information on each class is indicated. The validity and utility of several general rules and regularities are also examined. An appendix includes a table of rate coefficients for vibrational and electronic excitation and deexcitation reactions, taken directly from or derived from data in the literature. This table provides comprehensive coverage of some classes of reactions and representative coverage of the others.

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I. INTRODUCTION

When energy is deposited in a gas by shock heating, charged-particle bombardment, chemical reaction, or other means, significant amounts of rotationally, vibrationally, and electronically excited species are usually produced. These excited species may emit optical radiation, and may also by their subsequent reactions produce important effects on other observables, such as the electron density.

The situation is simplest when the gas is in "local thermodynamic equilibrium," that is, when the atoms, molecules, and ions at each point in the gas are distributed among the translational, rotational, vibrational, electronic, and chemical degrees of freedom according to equilibrium statistical-mechanical laws. In this situation the radiation or other properties of the gas can be calculated from its temperature or enthalpy, and pressure or density, using the basic thermodynamic and optical properties of its constituent chemical species. In the slightly more general case where all degrees of freedom except the chemical are in equilibrium, ordinary chemical reaction rates are also required. However, in many practical situations involving flames, discharges, afterglows, shock fronts, hypersonic flows, etc., especially at low densities, the vibrational and electronic degrees are also out of equilibrium. To analyze such situations, detailed reaction rates or cross sections for the production or destruction of specific vibrationally and electronically excited states are needed. Such rates are the subject of the present review.

More general situations, where even the translational or rotational distributions are non-Maxwellian, may also occur. However, only a few gas-kinetic collisions are required to establish translational or rotational equilibrium,(1,2) so that nonequilibrium in these modes usually occurs only for such short times or such low densities that optical radiation is likely to be negligible.*

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*An important exception is the fluorescence excited in gases by bombardment with particles having energies much higher than the thermal energies of the gas molecules. Such fluorescence is not considered in the present review.

Moreover, little is known about the effects of rotational excitation on most types of reaction rates. Finally, keeping track of the individual translational, rotational, vibrational, and electronic populations of each chemical species in a gas mixture becomes prohibitive even on a large computer unless only one or two species are involved, or unless other simplifications can be made. One such simplification is sometimes reasonable in gas discharges: the electron energies are approximated by one temperature and the heavy-particle translational and rotational energies by a different temperature. The reaction rates pertinent to this situation are simply the ordinary Maxwellian-averaged values, evaluated at the electron temperature for the reactions involving electrons, and at the heavy-particle temperature for the other reactions.* For the above reasons, translational and rotational excitation will seldom be mentioned in the subsequent sections.

The present review is also limited to gas temperatures up to 20,000°K. At higher temperatures the problems become simpler because all the molecules are rapidly dissociated and because many high-energy cross sections have been accurately measured or calculated. In contrast, quantitative information on several important types of low-energy processes has been so meager, until very recently, that previous reviews have usually stressed the high-energy region.

In the following discussion, emphasis is laid on the basic physical principles and their general implications; for theoretical derivations and most mathematical results the reader must refer to the references listed. However, Appendix B contains a table of published reaction rates for the production or destruction of specific excited states.

The references given in the body of this review are selective rather than comprehensive. They include the most pertinent earlier reviews, and papers presenting important new developments not adequately covered in those reviews.

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*Except for three-body reactions involving an electron and two heavy particles, which may depend upon both temperatures.

II. THE PRESENT STATE OF KNOWLEDGE OF LOW-ENERGY EXCITATION AND DEEXCITATION RATES

PRELIMINARY CONSIDERATIONS

Excitation and deexcitation reactions may involve electrons, atoms, or molecules. Molecules may have translational, rotational, vibrational, electronic, and chemical energy. Atoms have only translational, electronic, and chemical energy;* they can be considered as a special case of molecules. Free electrons have only translational energy, but it is not desirable to include them as a special case of molecules, since their much smaller mass and larger velocity gives them quite different properties at the low energies of present interest.

When one distinguishes between electron and heavy-particle translational energy, there are six different types of energy and thirty-six different simple kinds of energy transfer, as indicated by the matrix shown in Table 1. Table 1 also indicates the extent to which each process has been investigated theoretically or experimentally (at low energies). Because there is no fundamental difference between an energy-transfer process such as translation → rotation and its inverse, rotation → translation (see "Detailed Balance" in Section III), half of the nondiagonal elements of the matrix could be omitted, leaving twenty-one independent processes. However, the experimental problems of measuring a process and its inverse are often quite different, so each is treated separately in Table 1. Asterisks indicate where considerable additional information can be deduced from the available results for the inverse process.

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*It is possible to define the chemical energy of all atoms to be zero, but this is often inconvenient because it makes the chemical energy of most molecules negative.

Table 1

MATRIX OF ENERGY-TRANSFER PROCESSES

From	To	Electron	Atom or Molecule				
		Transl.	Transl.	Rot.	Vibr.	Elect.	Chem.
Electron	Transl.	B	A	B	B	A	B
Atom or Molecule	Transl.	C*	A	A	A	C*	B*
	Rot.	N*	C*	C	C	C	C
	Vibr	N*	A	C	B	C*	C
	Elect.	C*	B	N*	B	B	B
	Chem.	C*	A	C	C	C*	B

Note: The symbols indicate roughly the extent to which each process has been studied theoretically or experimentally: A = a great deal, B = some, C = a little, N = none, * = more information can be deduced from results for the inverse process.

Much of our information on some of these processes comes from theoretical calculations or beam measurements of cross sections as functions of collision energy. To convert these results to rate coefficients as functions of temperature, they must be integrated over the appropriate Maxwell-Boltzmann energy distributions. For reactions involving only atomic species this is straightforward (at least if the reactants are in their ground electronic states, or known excited states). Reactions involving molecular species, however, are complicated by the additional rotational and vibrational degrees of freedom. In beam experiments the target gas is usually at room temperature and thus in its lowest vibrational and lower rotational levels. The simplest way to apply the results of such experiments to high-temperature gases is to assume that the cross section is independent of rotational and vibrational excitation, but this may be an inaccurate assumption. Some improvement may be obtained by treating each vibrational level separately but continuing to ignore rotation. To analyze processes in high-temperature molecular gases by such a procedure, however, much more cross-section information is needed than is furnished by conventional beam experiments.

Before going on to consider in some detail the individual processes shown in Table 1, it is well to emphasize the limitations of any such simple classification scheme. In the first place, some of the headings, particularly "chemical", cover a wide variety of processes which have little in common. Even such a seemingly well-defined process as vibrational excitation by electron impact can take place either "directly" or via a temporary negative-ion state. In some ways the latter mechanism is more like electronic excitation, although it yields the same products as the direct process.

In the second place, many important reactions produce (or consume) more than one type of energy simultaneously, so that their appropriate position in Table 1 is not evident. Fortunately, there exists a kind of hierarchy among the types of energy listed: translational, rotational, vibrational, electronic, and chemical (in ascending order). If any of these types is involved on one side of a reaction, inclusion on the same side of types lower in the hierarchy often does not significantly complicate the process. For example, an electronic energy transfer may be accompanied automatically by a change in vibrational energy due to the Franck-Condon principle (see Section III); also, a chemical reaction is not changed in principle when the reactants are initially vibrationally or electronically excited.

Even though an important aim of this review is to aid in understanding optical emissions from gases, no processes directly involving photons will be treated. The reason for this omission is that the absorption or emission of a photon by an individual atom or molecule (not undergoing collision) is basically simpler than the reaction processes considered here, and has been adequately reviewed in several places.(3-6) Moreover, because radiation times (10^{-8} sec or greater) are so much longer than actual collision durations (10^{-14} to 10^{-11} sec), the only processes involving simultaneous collision and radiation that are of general significance are atom-atom and electron-ion radiative recombination, where photon emission is necessary in order to stabilize the resulting molecule or atom. These latter processes have also been reviewed,(7,8) as have their inverses, photodissociation(9) and photoionization.(10)

Of the twenty-one independent energy-transfer processes shown in Table 1, nine will now be dismissed rather quickly. Three of these involve simple exchange of translational energy, and their rates are determined by the well-known elastic cross sections for electron-electron, electron-molecule, and molecule-molecule impact. Except when the particle masses differ greatly (as with electron-molecule collisions) only a few collisions are required to establish a Maxwellian translational-energy distribution.

The other six involve rotational energy exchange or conversion. As already mentioned in the Introduction, the rates for such processes are generally of lesser interest because the transfer between heavy-particle translational and rotational energy is so rapid that in many nonequilibrium gaseous situations it is reasonable to assume a Boltzmannian rotational distribution and bypass the excitation-deexcitation details. Moreover, rotational excitation affects only the fine structure of optical emission and absorption.

Only two of the six rotational processes have been much investigated. For the first, rotational excitation by electron impact, theories have been developed for the direct excitation of polar(11) and nonpolar(12,13) molecules, as well as for resonance excitation via negative ion states.(14) The agreement with experiment is generally good.(15-17) However, virtually all the experiments involve only energy-loss measurements on the electrons, so the comparison is limited to the fractional eV range where rotational excitation is the dominant energy-loss mechanism. Except for measurements of combined vibrational-rotational resonance excitation,(14,18) essentially no data are available for rotational excitation at electron energies near and above 1 eV, where some of the theories are expected to be poor.(11)

The theory of the second process, rotational excitation by heavy particle impact, has recently been reviewed by Takayanagi.(19) Its practical application is limited by mathematical complications and the lack of accurate angle-dependent intermolecular potentials. Considerable experimental information on this process is available, from measurements of ultrasonic dispersion and shock-wave structure.(1,2,20,21)

It is found that molecular rotation generally reaches thermal equilibrium in 5 to 10 gas-kinetic collisions, except for H_2, which requires several hundred collisions.

Very little is known about the remaining four processes involving rotational energy: rotation-rotation exchange, rotation-vibration transfer, rotation-electronic transfer, and the role of rotational energy in chemical reactions.(1,2,22) These processes will not be discussed further here.

In the balance of this section the remaining thirteen processes will be discussed in more detail. Generally they will be treated in groups, corresponding to rows or columns of Table 1.

ELECTRON-IMPACT PROCESSES

A well-established theory is available for calculating vibrational excitation by low-energy electrons, but it often gives cross sections too low to explain the energy losses observed in diffusing electrons.(11-13,15,17) Recently, this discrepancy has been explained by the observation of negative-ion resonances in H_2, N_2, and CO near 2 eV, which greatly increase the probability of vibrational excitation.(18) A resonance theory has been developed which fits the measurements fairly well when certain parameters are properly adjusted.(14,23,24) At present the theory and experiment are complementary, since the parameters cannot be calculated theoretically with sufficient accuracy (except perhaps for H_2), but the theory does give absolute cross sections, while most measurements are only relative. Direct electron-beam measurements have been made only on H_2, N_2 and CO.(18) Electron diffusion or swarm data are available on several other molecular gases but their interpretation is somewhat ambiguous because of the energy spread of the swarm, unless they can be combined with other data.(16,25)

Electronic excitation produced by low-energy electrons can be calculated approximately by classical methods,(26,27) with results that usually agree with measurements within a factor of 2 or 3. The agreement is often poorer near the threshold energy, however, which is the important region for thermal electrons. More accurate quantum-mechanical calculations have also been carried out for a number of electron-excitation cross sections involving light atoms.(28-31) Their agreement with experiment ranges from fair to excellent, depending upon the complexity of the atom and the validity of the approximations made in the theoretical treatment. Experimental excitation cross sections are available for many noble-gas and alkali-metal atoms, a few other atoms (H, Fe, Ba, Hg, and Tl), and several molecules (see Appendix B).(32)

In measurements of electron-impact cross sections (as well as beam measurements of heavy-particle cross sections) the target gas is usually at room temperature. Thus, results are obtained only for atoms and molecules in their ground electronic and vibrational state. Deexcitation or "super-elastic" cross sections may be obtained from these by detailed balance (see Section III) provided that the final state is the ground state. However, deexcitation to lower excited states is often important, especially for molecular gases with their low-lying excited vibrational levels. Fortunately, gas discharges and other means can be used to measure rates or cross sections for excited states, though thus far such measurements have been made only for a few rare-gas and metallic atoms.(33-35)

An electron-impact-chemical process likely to produce excited states is dissociative recombination of molecular ions. Recently, Zipf(36) has found that a large fraction of the oxygen atoms produced in the reaction $O_2^+ + e \rightarrow O + O$ are in excited ^1D and ^1S states. This may also hold for recombination of many other molecular ions. A theory of dissociative recombination is available,(8) but numerical results depend upon accurate repulsive molecular potential curves, which are not yet available. The closely-related process of dissociative attachment may also produce excited states. However, for the important case of $O_2 + e \rightarrow O^- + O$, the measured total cross section agrees well with a theory that assumes unexcited products.(37)

Excited states are often produced when molecules are dissociated by electron impact. For O_2 in the 7 - 10 eV region production of

$O^*(^1D)$ is highly likely, judging by the analogous ultraviolet dissociation process. Semiquantitative data is available on many molecules for dissociative ionization yielding excited products. The energy thresholds, however, are usually too high to make these processes significant in the temperature range under consideration here.

Three body collisional-radiative recombination of atomic ions will also yield excited states of neutral atoms, in amounts that can be calculated approximately from the theory of Bates, Kingston and McWhirter.(8,38) Ion-ion recombination may also yield excited states, but no relevant data are available.

An excited ion may be effectively quenched by recombination. However, in most situations recombination is probably slower than other types of quenching. This follows from the small rate coefficient for recombination of atomic ions, and the usually small fractional ionization when molecular ions are important.

EXCITATION AND DEEXCITATION BY ATOMIC OR MOLECULAR IMPACT

Collisions where the kinetic energy of an atom or molecule is converted to vibrational energy (and the inverse deexciting collisions) have frequently been treated theoretically,(20,21,39) though generally approximations are made that are rather hard to justify.(40) The theoretical results, calculated using intermolecular potentials from virial or transport-property measurements, usually agree within a factor of 5 with the rather extensive volume of experimental data.(1,20,21) Better agreement can be obtained by the empirical procedure of using some vibrational relaxation data to adjust the intermolecular potentials.

Collisions involving conversion of translational energy to electronic energy (or vice versa) can be treated formally by theories involving potential-curve crossing.(41-44) Unfortunately, except for a few of the very simplest cases, potential-energy curves sufficiently accurate to make quantitative predictions are not now available. The Rydberg-Klein-Rees method(45) of determining potential curves is seldom helpful here because it is limited to two atoms colliding on an attractive curve in a region where spectroscopic data are available.

However, in cases involving only two light atoms there is some hope of obtaining accurate potential curves in the next few years from quantum-mechanical calculations using high-speed computers.

Only a few experiments, done with shock tubes, have given absolute rates for the conversion of translational to electronic energy at low energies.(46-48) For the reverse process, experiments on radiation quenching provide a considerable amount of data which may be pertinent.(1,41-43) However, detailed determination of the states of the quenching products is seldom made. Without such determination, one cannot be confident that the electronic energy is actually converted into translational energy unless the electronic energy is too small to produce vibrational excitation (as in quenching of the higher spin-orbit substates of a ground state), or only atoms with no other low-lying electronic states are involved.

VIBRATIONAL AND ELECTRONIC EXCITATION TRANSFER

The theory of vibrational exchange in molecular collisions has been described in detail by Herzfeld and Litovitz.(20) The theoretical results usually agree with the experimental data within a factor of 5. The calculations are quite sensitive to details of the intermolecular potential, and can be improved by using potentials based partly on vibrational relaxation data. The available experimental data are quite extensive; moreover, further work is currently being carried out at several laboratories.

Theories of electronic-energy exchange and of vibrational-electronic energy conversion generally require a knowledge of the potential-energy surfaces, and therefore are of limited practical value. Experimentally, the many cross sections for quenching of Na^*, Hg^*, and Cd^* may be pertinent.(1,41-43) For molecular quenchers with cross sections much larger than those of atomic quenchers and dissociation energies too high to permit dissociation it has generally been believed that most of the energy goes into vibrational excitation. However, very recent measurements by Polanyi and colleagues(49,50) show that, at least in the $Hg^* + CO$ and $Hg^* + NO$ systems, seldom if ever does all of the energy go into vibrational excitation. By detailed balance (see Section III), the excitation of Hg by vibrationally-excited CO or NO should then be very slow at low temperatures, at least when barely enough vibrational energy is available,(49) in contrast to observations by Starr(51) and Fite(52) of fast Na and K excitation by $N_2^\dagger$. A few rates for N_2^*, N_2^{+*}, O^*, and O_2^* quenching are also available,(53-56) but the products are not identified. Recent work on noble-gas mixtures (with laser applications) provides practically the only unambiguous quantitative data for electronic excitation transfer.(1,57,58)

Penning ionization, where a highly-excited atom or molecule ionizes a colliding particle of lower ionization energy, is actually just a case of excitation transfer where the final electronic state is in the continuum. Penning ionization has been observed in a large number of mixtures;(59,60) unfortunately, however, quantitative rates are available only for reactions involving He^*, Ne^*, and Ar^*. The measured rates frequently approached gas-kinetic, indicating that this process can be an important deexcitation mechanism for highly-excited states in gas mixtures. Conversely, Penning ionization may also produce vibrationally or electronically excited states, as shown by the qualitative observations of Cermak.(61)

EXCITATION OR DEEXCITATION BY CHARGE TRANSFER

Theory indicates that at thermal energies charge transfer is likely to take place to near-resonant states (see Section III). Accordingly, excited products should often result from charge transfer. This conclusion is supported by the published experimental data at higher energies.(62-64) No quantitative excitation measurements are available at thermal energies, but the large total charge-transfer rates often found at room temperature(65) and the existence of excited states with near-resonant energies, make such excited products very probable.

Atoms, molecules, or ions can also be deexcited by charge transfer.(66) In fact, this may often be the dominant quenching mechanism for excited ions. It will usually be less important in deexciting neutral particles, however, because the latter require charged collision partners, which are less abundant than neutral particles in most situations of interest.

CHEMICAL EXCITATION AND DEEXCITATION (INCLUDING ION-MOLECULE REACTIONS)

Chemical reactions are often among the most important sources of excited species in nonequilibrium gases. The significance of chemical reactions in deexcitation is less clear, but they may be important for some species. Unfortunately, general theoretical principles (see Section III) seldom provide much information on chemical reaction rates, so each rate must be measured experimentally. To be sure, a theory based on potential energy surfaces for the reacting atoms or molecules can be developed formally, but except for a few of the simplest systems the potential energy surfaces can seldom be determined with sufficient accuracy even to make valid order-of-magnitude predictions for reaction rates.(43) Some recent work(67,68) has been done on the inverse process, adjusting potential energy surfaces to give the observed reaction rates. Recent developments in computer codes for molecular quantum-mechanical calculations may also lead to potential energy surfaces of useful accuracy.

Experimental measurements are available for a number of chemical reactions producing excited species. The most-studied are the atom-recombination reactions which produce the well-known nitrogen, oxygen and air afterglows.(69) Unfortunately, these afterglows are quite complex, involving a variety of excitation, deexcitation and excitation-transfer processes, and many of the details are still debatable. Moreover, very few data are available at elevated temperatures. Somewhat better understood are the NO + O and CO + O chemiluminescent reactions, because they appear to involve fewer elementary processes and because recent investigations have established their temperature dependence.(70,71) It might be mentioned that over the pressure range of usual interest these reactions behave approximately like two-body excitation reactions, and only the fact that the rate varies with the type (but not the concentration) of inert diluent, and a few other minor effects, shows that a steady-state combination of three-body excitation and two-body quenching actually prevails. The history of reaction-rate measurements in afterglows and flames contains many such examples where the initial results could be nicely explained by a simple mechanism, but later results over a wider variety of conditions demonstrated that the mechanism must be more complex.

A few other electronic excitation rates in nitrogen-oxygen systems, and also a few involving H, OH, C_2 and CN, have been measured. For excitation of metals only the recent flame measurements of $H + OH + K \rightarrow H_2O + K^*$, $O + O + Na \rightarrow O_2 + Na^*$, and $H + H + Na \rightarrow H_2 + Na^*$, reaction are at hand.(72,73) Moreover, the coefficient quoted for the second reaction (1.5×10^{-29} cm^6/sec) is more than an order of magnitude faster than is reasonable for a fast three-body reaction, indicating that the actual mechanism may be more complex, and that the measured coefficient cannot be safely used for gas mixtures containing diluents different from those in the flame investigation.

Absolute cross sections for chemical reactions yielding vibrationally excited species have been measured for a number of alkali halide reactions (using crossed beams),(22) and for $N + NO \rightarrow N_2^{\dagger} + O$,(74,75) but apparently for no other reactions.

Quantitative information on deexcitation by chemical reaction is available only for a few reactions involving electronically-excited O, Cd, Hg, NO, and O_2, plus some reactions of the type $He^* + He \rightarrow He_2^+ + e$. The rates for such reactions are frequently quite large (see Appendix B).

III. RULES AND REGULARITIES

INTRODUCTION

Since the rates or cross sections for many excitation reactions of practical interest are not known, it is desirable to examine existing theory and experiment for any general principles which can aid in estimating unknown rates.

Almost too obvious to mention is the principle that in any collision (elastic or inelastic) between particles the total energy, linear momentum, and angular momentum must be conserved. Conservation of energy implies that endothermic reactions have a kinetic-energy threshold below which the cross section vanishes,* and consequently that the corresponding thermal reaction rate will be very small when the threshold energy is large compared to the mean thermal energy. The implications of conservation of linear and angular momentum concern mostly the translational and rotational energy distributions of reactants and products, which will not be discussed further here.

Some attempts have been made to estimate the relative rates of different reactions simply from the relative statistical weights of possible products. However, many other factors besides statistics determine the reaction rates, and for the atoms and small molecules of greatest interest in heated gases these other factors may vary by orders of magnitude, overwhelming any statistical factors. Only for complex molecules having many reaction channels is the statistical-weight approach plausible.

Although a few general rules for reaction rates will be discussed below, it may be pointed out there that these rules do not have the general validity and usefulness of the familiar selection rules for photon absorption and emission. Reaction-rate rules usually indicate only tendencies for certain reactions to be fast or slow, and there are known exceptions to virtually all of their predictions.

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*Some exothermic reactions also have thresholds, due to potential-energy barriers.

THE WIGNER SPIN-CONSERVATION RULE

In light atoms, and molecules composed thereof, the coupling between electron spin and other degrees of freedom of the molecule (including electron orbital motion) is very small, amounting typically to a few thousandths of an eV for atoms like nitrogen, or a few hundredths of an eV for those like argon. Thus, it is improbable that in an electron-molecule or molecule-molecule collision the total spin will change.(42) For example, in the exothermic reaction $N(^4S) + NO\ (^2\Pi) \rightarrow N_2\ (^1\Sigma) + O(^3P \text{ or } ^1D)$, the reacting N and NO have spins of 3/2 and 1/2, respectively, which combine to give a total spin of either 1 or 2, depending upon their relative orientation. If the atomic O is produced in the ^3P state, the total spin of the products will be 1, so that spin can be conserved. For production of $O(^1D)$, however, the final spin will be zero, and spin cannot be conserved. Thus, the latter reaction is expected to be slower than the former by two to four orders of magnitude (other factors being equal). Similar arguments may be applied to $N_2(^1\Sigma) + e \rightarrow N_2^*\ (^3\Sigma \text{ or } ^5\Sigma) + e$ to show that excitation to the triplet state is "permitted" but that to the quintet state is "forbidden."

Unfortunately, the spin-conservation rule is not as useful as it might at first seem. In the first place, though it indicates that reactions not conserving spin are slow, it cannot show that spin-conserving reactions are fast, because energy barriers, "steric" (orientation) factors, or other effects may make the latter slow also. Moreover, because of the several ways the spins of the individual reactants or products can combine (except when one spin is zero), the rule is usually not very restrictive. Finally, a few cases of fast reactions which do not conserve spin appear to be well-substantiated experimentally. These include:

$$He(n\ ^1P) + He\ (1^1S) \rightarrow He\ (1^1S) + He(n\ ^3F)$$

and

$$O^+(^4S) + CO_2\ (^1\Sigma) \rightarrow CO\ (^1\Sigma) + O_2^+\ (^2\Pi),$$

both of which have cross sections near gas-kinetic.(58,76) The breakdown of spin conservation in the first reaction is due to the small energy difference between the He(n ^3F) and the He(n ^1F) levels, which allows a mixing of the two states.(77) For the second reaction, however, such an explanation does not appear to be applicable. Instead, it may possibly be due to spiralling collision trajectories which allow the reacting particles to remain close to each other long enough for a spin-forbidden transition to take place, especially since recent information on spin-forbidden predissociations(78) indicates that such transitions are not as slow as once thought.

ADIABATICITY, CURVE CROSSING, AND ENERGY RESONANCE

When two or more atoms or molecules collide with relative velocities very small compared to the orbital velocities of their electrons, the electrons have time to adjust to the instantaneous positions of the atomic nuclei, so that the electronic energy depends only upon the relative positions of the nuclei. (This simplification is known as the Born-Oppenheimer approximation; it applies not only to slow molecular collisions but also to the rotational and vibrational motion of the nuclei within a single molecule.) Accordingly, the atomic nuclei can be regarded as moving on a potential-energy curve (or surface, if more than two nuclei are involved so that more than one independent variable is required to specify their relative positions). Typical potential curves for two different initial electronic states are shown by the solid curves AB and A'B' in Figure 1. Such slow collisions involving no electronic transitions are often called "adiabatic." It is apparent that adiabatic collisions between two atoms will be elastic, the atoms finally coming apart in their original states, unless energy is removed by a third particle or by radiation. Adiabatic collisions involving polyatomic molecules, however, may result in rotational or vibrational excitation or chemical reaction.

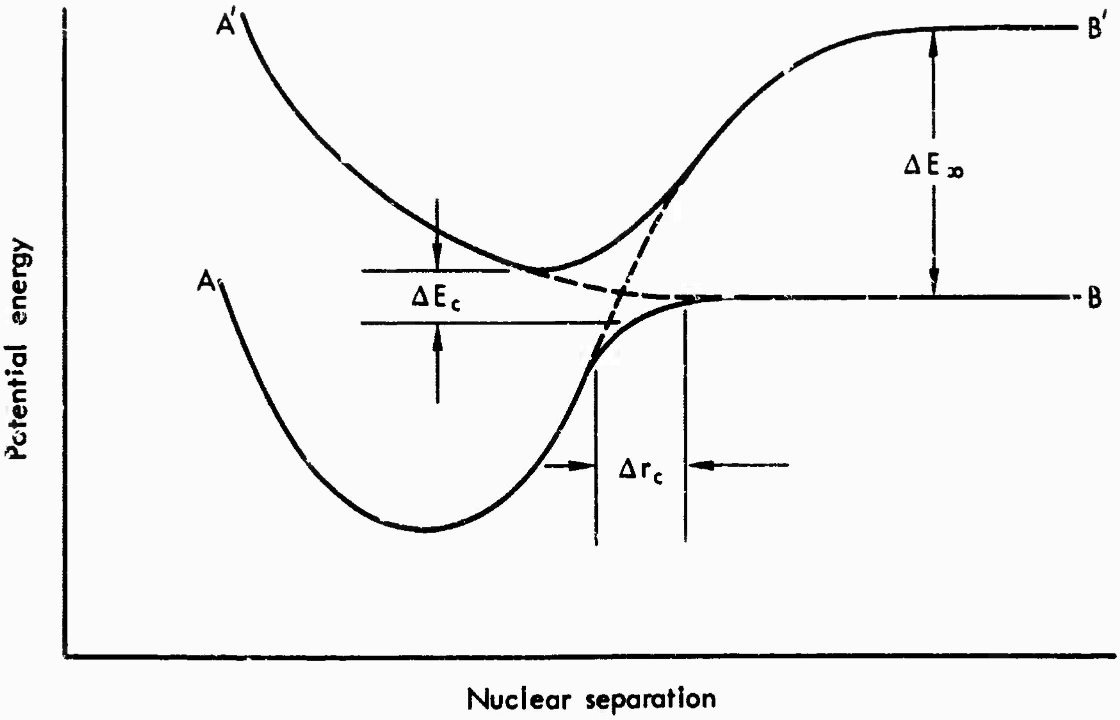

Fig. 1--Pseudocrossing of potential energy curves

Frequently, as two nuclei follow a curve from B to A (Fig. 1) a considerable rearrangement of the orbital electrons is required, while at small internuclear separations there is another state, A', much closer in electron configuration to B than A is. Consequently, in collisions too rapid to permit the electrons to readjust, the nuclei follow the broken curve BA'. Of course, on the way out the relative velocity is still high so the nuclei follow the broken curve back to B, and the collision is again elastic. To produce a permanent electronic transition from B to B' the nuclei must follow the solid curve on the way in and the broken curve on the way out, or vice versa. Hence, the excitation cross section will have a maximum at some intermediate velocity where the probabilities of following the solid or broken curves are equal. Quantum-mechanical considerations(42) show that this condition is satisfied when the time spent in the cross-over region, $\Delta r_c/v$, is roughly equal to the characteristic time for the energy change required, $h/(2\pi \Delta E_c)$, where Δr_c and ΔE_c are defined in Fig. 1, and h is Planck's constant. The velocity corresponding to maximum cross section is then approximately $2\pi \Delta E_c \Delta r_c/h$, and at this velocity the cross section may approach gas-kinetic.

The question of exactly what constitutes an adiabatic collision (where the electronic state remains "the same" throughout the collision) can often be answered only in the context of a particular collision velocity range.(43) If the two potential curves belong to the same species, e.g., both $^2\Pi$, electronic interactions generally prevent them from approaching each other very closely, and any atomic collision with energies below the keV range is virtually certain to follow adiabatically either the lower or the upper curve. On the other hand, curves for states of different type, like $^1\Sigma$ and $^3\Pi$, may appear to cross, but interactions in a very small region near the apparent crossing will prevent an actual crossing (in the low-velocity limit) and give instead an upper and a lower curve, similar to the solid curves of Fig. 1, but almost touching. Each curve then represents an "electronic state" which is $^1\Sigma$-like at small and $^3\Pi$-like at large internuclear distances, or vice versa. However, the curves come so close to crossing that, even at collision velocities as low as room-temperature thermal velocities, the nuclei will usually follow one of the broken curves in Fig. 1, "crossing over" to stay always on a $^1\Sigma$ or on a $^3\Pi$ curve.[*] Such collisions are sometimes called adiabatic, but strictly speaking they are diabatic (nonadiabatic).(43)

In many cases, especially where ΔE_∞ is large, as in collisional ionization, there may be no pseudocrossing of the curves, or even no region where the curves come relatively close together. However, there may still be an appreciable possibility of making a transition between the two curves while the nuclei are within some distance b where their orbital electrons interact significantly. This transition will be most probable when the collision time, b/v, is roughly equal to the characteristic time, $h/2\pi\ \Delta E(b)$, for making such a transition. In the last expression, $\Delta E(b)$ is the mean energy difference between the curves in the neighborhood of b; it is often approximately equal to ΔE_∞ unless both of the colliding particles are charged. The velocity which maximizes the cross section is then given by

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[*] Even near absolute zero this statement holds, since if the initial curve is even slightly attractive the velocity at the pseudocrossing point will be increased beyond the adiabatic limit, while if it is even slightly repulsive few collisions will have enough energy to reach this point.

$$v_{\max\,\sigma} \approx 2\pi b\ \Delta E(b)/h$$

which is very similar in form to the expression obtained for the pseudocrossing case. If the electronic configurations for the two curves are not too different (same total spin, etc.) the maximum cross section may approach gas kinetic.

For a distance b of a few Angstroms and an energy difference $\Delta E(b)$ of a few eV, the above expression yields a velocity of about 10^8 cm/sec, corresponding to an energy of about 100 keV for an N or O atom. In the energy range of present interest, 0 to 25 eV, the excitation cross sections will, therefore, be very small except when the potential curves for the two states approach each other very closely, as in a pseudocrossing. Such a close approach is most likely to occur when ΔE_∞ is very small, that is, when there is a close energy resonance between the initial and final states. However, energy resonance is neither a necessary nor a sufficient condition for a large cross section at thermal energies. It is not necessary because, even when the initial and final potential curves are far apart at large internuclear distances, the curves may approach closely at some smaller internuclear distance. It is not sufficient because the opposite behavior may occur: even when the curves are very close at large internuclear distances they may diverge at the smaller internuclear distances where the transition could take place.

The above statements are supported by recent detailed measurements on exothermic chemical(22) and quenching reactions,(49,50) which show that often a considerable fraction of the reaction energy goes into translational energy, with correspondingly less internal excitation of the products, even when higher, near-resonant states of the products are available.

THE FRANCK-CONDON PRINCIPLE

When an electron of a few eV or more collides with a molecule and causes an electronic transition, the electron velocity is very rapid compared to the vibrational motion of the molecule, so that afterwards the nuclei of the molecule still have nearly the same relative position and velocity as before the transition. This principle is illustrated for a diatomic molecule in Fig. 2. When the molecule is in the lowest vibrational level of its ground electronic state, corresponding to the point A, and is excited to the next electronic state, it is most likely to go to the point B, resulting in the indicated vibrational excitation of this state. When excited to the higher, repulsive state it will go to the point C and the molecule

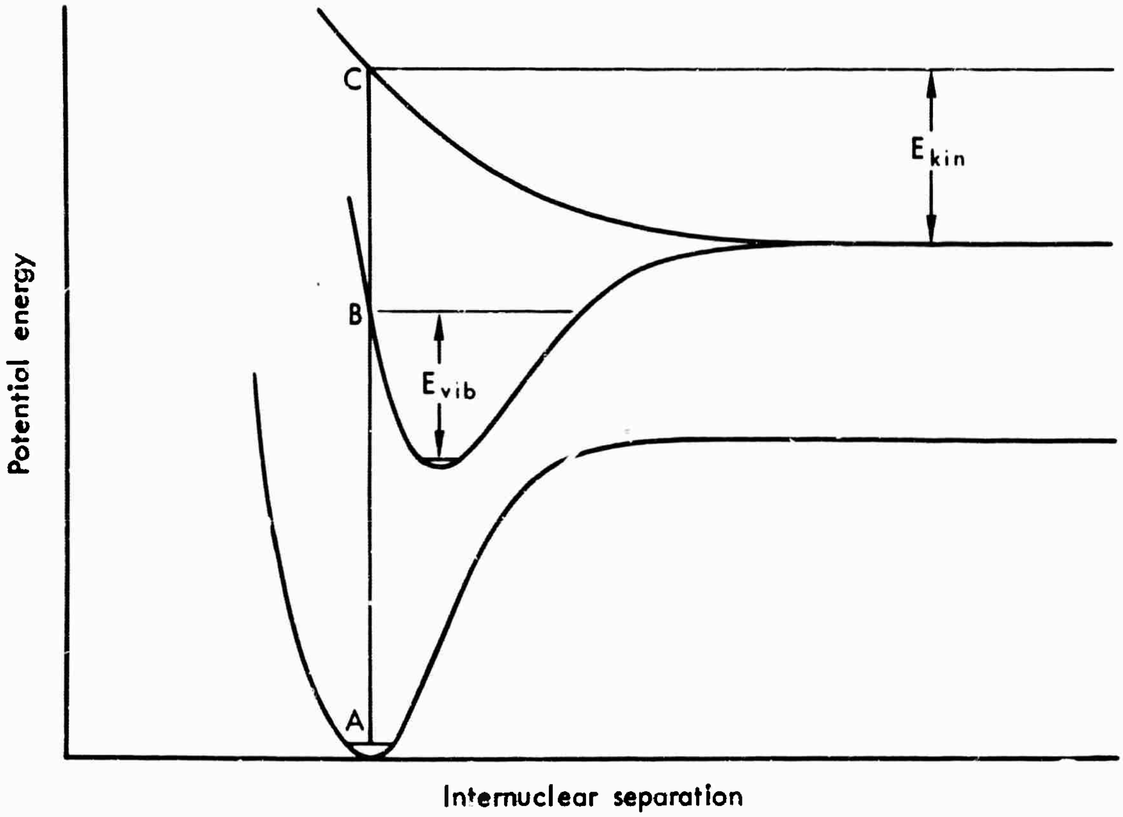

Fig. 2—Potential energy curves and the Franck-Condon principle

will dissociate with the indicated kinetic energy distributed between the two atoms. The same principle applies to the inverse, deexciting collisions, and also to transitions between two excited states, or transitions to a state of the ion (i.e., ionization by electron impact).

A more accurate, quantum-mechanical treatment of the problem shows that there is still a finite, though small, probability of going to points some distance from B or C. Relative probabilities for going to various vibrational levels, known as Franck-Condon factors, have been calculated and are available in the literature(4,5) for many important transitions (usually in connection with photon processes, to which they also apply).

There are several significant limitations to the use of Franck-Condon factors for electron-impact excitation or ionization. First, as already mentioned, the electron velocity must be large compared to vibrational velocities, but this is usually satisfied even by fractional eV electrons. Second, and more restrictive, the electron energy both before and after collision must be large compared to the energy variation over the vibrational levels of interest, so that near-threshold effects do not distort the probabilities. Third, the electronic part of the transition probability must not vary significantly with internuclear distance. This variation has been studied in connection with photon processes; usually it is not great.(5) Finally, a practical limitation is that excitation or ionization must not proceed through an intermediate state, or the Franck-Condon factors for a single transition will not give the correct vibrational distribution. This is especially important for electron-impact ionization, because highly-excited states of the neutral molecule often overlap and autoionize to states of the molecular ion.

There is recent evidence that Franck-Condon factors are also applicable, at least approximately, to low-energy reactions involving Penning ionization, charge transfer, and electronic energy transfer.(61,66,79) Such a result seems reasonable for reactions with such large cross sections that the atoms effectively "brush by" without transferring a significant amount of their kinetic energy into vibrational energy.

DETAILED BALANCE

When a gas is in equilibrium, the principle of detailed balance says that the rate of production of any species in any particular state by any particular process is exactly equal to its rate of destruction by the reverse process. The specification of "state" may be as detailed as desired; it may be narrowed to a particular rotational and vibrational level and even to a particular translational velocity interval of each of the reactants. Since detailed balance applies to each microprocess, simple summation shows that it also applies (in equilibrium situations) to overall processes such as chemical reactions where no distinction is made between the different internal states of the reactants or products.

In a gas the reaction rate is proportional to the product of the concentrations of the reactants, with a proportionality constant k which depends upon the temperature and possibly on other system parameters. For any reaction, such as

$$A + B \rightleftarrows C + D,$$

detailed balance gives the equilibrium condition

$$(k_f)_{eq}\ (A)_{eq}\ (B)_{eq} = (k_b)_{eq}\ (C)_{eq}\ (D)_{eq},$$

where k_f and k_b are the forward and backward reaction coefficients, (A), (B), etc., are the respective concentrations, and the subscript eq indicates the equilibrium value. From thermodynamics,

$$\frac{(C)_{eq}\ (D)_{eq}}{(A)_{eq}\ (B)_{eq}} = K_{eq},$$

where k_{eq} is the equilibrium constant, which depends only on the temperature. Hence

$$(k_f)_{eq} \;/\; (k_b)_{eq} \;=\; K_{eq} \;; \qquad (1)$$

i.e., in equilibrium the ratio of forward to backward reaction coefficients is equal to the equilibrium constant.

However, a reaction coefficient has practical significance and is measurable only in nonequilibrium situations. To measure a reaction coefficient, one starts with a relative excess of reactants or deficiency of products. Among each reactant species there will always be particles with a range of velocities, and usually with a range of rotational, vibrational, or electronic levels. Generally some of these levels will be more reactive than others. In the nonequilibrium situation the more reactive levels will be removed (by reaction) more rapidly than the others, resulting in a quasi-steady internal distribution of levels in each reacting species which makes it less reactive than if it had an equilibrium distribution.(80) Accordingly, the measured reaction coefficient will always be less than the equilibrium value. However, if the rate of energy redistribution among the internal states is fast compared to the reaction rate, the rate coefficient will have nearly its equilibrium value.

Detailed theoretical investigations have been carried out for dissociation reactions, where it is reasonable to assume equilibrium distributions for translational and rotational energy, but not for vibrational energy, because the latter is coupled into the dissociation process. The results show that when the mean thermal energy is much less than the dissociation energy the dissociation and association coefficients are only slightly smaller than their equilibrium values.(81,82) Moreover, both coefficients are decreased by the same fraction, so that Eq. (1) still holds. A recent investigation of chemical exchange reactions, however, shows that deviations from this relation may be important in this type of reaction.(83)

When the vibrational or electronic energies of a species are not in equilibrium, it may be desirable to treat each vibrational level or electronic state as a separate subspecies, with its own reaction rates. Such a procedure permits use of detailed balance even in quite nonequilibrium situations, as long as the translational and rotational modes are in equilibrium, and it gives excited-state populations directly. On the other hand, it makes the analysis more complicated, and greatly increases the number of reaction rates which must be known before the overall process can be calculated.

LIMITED RULES AND REGULARITIES

The inadequacy of general rules and regularities for estimating unknown reaction rates has been indicated above. Recent experimental and theoretical results, however, suggest that more limited rules and regularities, restricted to specific types of molecules and classes or subclasses of reactions, may permit such predictions. For example, Millikan and White(84) were able to fit, within a factor of 2, data on vibrational-translational energy transfer for many diatomic molecules by a simple function of the vibrational energy interval, reduced mass, and temperature. (Their result, converted to a reaction coefficient, is listed in Appendix B.) Moreover, in the field of chemical processes, recent measurements of reactions between alkali atoms and various halides indicate that these can be grouped into rebound, stripping, and intermediate reactions, and that the properties of each type can be characterized fairly completely.(22) Similarly, the rates for conversion of the spin-orbit electronic energy of excited alkali atoms into translational energy by collisions with rare-gas atoms follow a fairly simple pattern.(85)

Other patterns for other cases have emerged or are beginning to emerge. However, because of the large number and complexity of these patterns, and the incompleteness of our present knowledge, no attempt will be made to summarize them here.

Appendix A

CLASSIFICATION OF REACTIONS LEADING TO EXCITATION, DEEXCITATION, OR EXCITATION TRANSFER

In listing a large number of specific excitation and deexcitation reactions, as in Appendix B, it is desirable to order them by some systematic classification scheme. One approach to such a scheme has already been outlined in Section II. Specifically, such reactions may be grouped by their type of energy source or sink: translational, rotational, vibrational, electronic, or chemical. As explained earlier, it is also desirable to make a distinction between the translational energy of a free electron (as in electron-impact processes) and that of an atom or molecule. On the other hand, a reaction and its reverse logically belong in the same group. To include reactions where several types of energy participate simultaneously, without introducing a large number of additional groups, one can use the natural hierarchy of energy types: translational, vibrational, electronic and chemical (in ascending order). When any particular type is involved on one side of a reaction, inclusion on the same side of types lower in the hierarchy usually does not change the basic process. Rotational energy, which does not fit easily into this hierarchy, is generally omitted from this review, for reasons explained in Section II.

The above considerations lead to a few broad reaction groups. For many purposes a subdivision of these into more specific categories appears desirable. A logically consistent subdivision, however, proves difficult. Taking a strictly empirical approach, one could easily write down several dozen distinct reaction categories, which differ in the number of reacting or product particles, their charges and vibrational and/or electronic excitation, and the number of chemical bonds formed or broken. In view of the present state of knowledge of excitation rates, however, such a list is undesirably long, approaching in length the list of known rate coefficients. Ideally, each category should be large enough to include several reactions on which quantitative data are available, but small enough so that only very similar reactions are included. In the classification scheme presented below, this goal has been attempted by using the "hierarchy principle" to combine reactions, but making a practical distinction between two-body and three-body reactions, even though one is sometimes the reverse of the other. Moreover, some distinctions are made on the basis of the electric charges of the particles (such as between dissociative recombination and dissociative attachment), although in electron-impact excitation and in chemical (including ion-molecule) reactions the charge is ignored.

The present approach might seem less desirable than a theoretically-consistent scheme. One fairly typical example, however, will show the difficulties in the latter approach: The vibrational excitation of N_2 by 3-eV electrons is known to take place through formation of an unstable N_2^- state; thus, this process theoretically belongs in the same (or neighboring) category with dissociative attachment to O_2 (which takes place through unstable O_2^-) and in a quite different category from the "direct" vibrational excitation of N_2 by 1-eV electrons. A classification scheme based on such theoretical considerations, however, would be very confusing to many users.

In the classification scheme given below, the following notation is used:

A,B,C,D,	Atoms or molecules (may often be excited or ionized, even when not specifically designated, without affecting the classification of the reaction)
$\dagger$	Superscript for vibrational excitation
$*$	Superscript for electronic excitation (may also be vibrationally excited)
$\dagger,*$	Superscript for either vibrational or electronic excitation (or both)

Usually a reaction and its reverse are not listed separately; where a reverse is referred to later it is designated by the reaction number followed by a prime (').

TWO-BODY REACTIONS

1. Electron-impact reactions and electron-ion recombination

a). $e + A \rightarrow e + A^{\dagger}$

b). $\rightarrow e + A^{*}$

c). $\rightarrow 2e + (A^{+})^{\dagger,*}$

d). $e + AB \rightarrow e + A^{\dagger,*} + B$

e). $e + AB \rightarrow A^{\dagger,*} + B^{-}$

f). $e + AB^{+} \rightarrow A^{\dagger,*} + B$

2. Heavy-particle reactions (including ions)

a). $A + B \rightarrow A^{\dagger} + B$

b). $A^{\dagger} + B \rightarrow A + B^{\dagger}$

c). $A + B \rightarrow A^{*} + B$

d). $A^{\dagger} + B \rightarrow A + B^{*}$

e). $A^{*} + B \rightarrow A + B^{*}$

f). $A^{\dagger,*} + B \rightarrow A + B^{+} + e$

g). $A^{\dagger,*} + B \rightarrow AB^{+} + e$

h). $A^{\pm} + B \rightarrow A^{\dagger,*} + B^{\pm}$

i). $A^{-} + B^{+} \rightarrow A^{\dagger,*} + B$

j). $A + B \rightarrow C^{\dagger,*} + D$

k). $A^{-} + B \rightarrow AB^{\dagger,*} + e$

THREE-BODY REACTIONS

3 Electron reactions

a). $e + A^{+} + e \rightarrow A^{\dagger,*} + e$

b). $e + A^{+} + B \rightarrow A^{\dagger,*} + B$

c). $\rightarrow A + B^{\dagger,*}$

4. Heavy-particle reactions (including ions)

a). $A + B + C \rightarrow AB^{\dagger,*} + C$

b). $\rightarrow AB + C^{\dagger,*}$

c). $A^{-} + B^{+} + C \rightarrow AB^{\dagger,*} + C$

d). $\rightarrow AB + C^{\dagger,*}$

Appendix B

A TABLE OF MEASURED OR CALCULATED RATE COEFFICIENTS FOR SPECIFIC EXCITATION OR DEEXCITATION REACTIONS

The table on the following pages summarizes much of the quantitative data published on excitation and deexcitation rate coefficients at temperatures up to 20,000°K. However, it usually lists only reactions where the identities of the reacting and product species, including the vibrational and electronic states of the reactants, can be established with reasonable confidence. Where more than one rate has been published for the same reaction, our assessment of the "best value" (which may be an average of different investigators' results) is listed here.

Because of the wealth of data on electron-impact excitation and heavy-particle vibrational excitation, only a selective rather than a comprehensive listing of these rates is presented here. Rates of excitation for many of the less common atoms and molecules, as well as for higher excited states of the more common species, have been omitted. Other electron-impact data may be found by referring to the comprehensive bibliography prepared by Kieffer,(32) and to an extensive review of electron-impact excitation of atoms currently under preparation by S. J. Smith and B. L. Moiseiwitsch at the Joint Institute for Laboratory Astrophysics, University of Colorado. For heavy-particle vibrational excitation, data up to 1961 have been reviewed by Cottrell and McCoubrey,(21) while some more recent results are summarized in the graphs and tables of Millikan and White.(84)

Many rate coefficients for quenching of electronic or vibrational excitation have been measured, but the table lists primarily those for which one knows whether the bulk of the energy goes into vibrational, electronic, or chemical energy of the products. (As pointed out earlier, it is not safe to assume that molecular quenchers yield primarily vibrational excitation.) A few quenching coefficients without identification of products are listed at the end of the two-body reactions, under the label "2Q." These coefficients are clearly of lesser value, since one does not know what fraction of the energy is degraded into translational energy and what fraction is simply transferred to other excitational or chemical energy, and thus still available for subsequent reactions. Many additional quenching cross sections may be found in the literature.$^{(1,41-43)}$ Incidentally, one should note that the quenching "cross sections" published in many older papers and even a few recent ones are actually collision diameters squared, and are thus smaller by a factor of π than the cross sections as usually defined.

For similar reasons, the many reactions which are known to produce some vibrationally or electronically excited molecules,$^{(86-89)}$ but in unknown proportions, have been omitted.

Published results of beam measurements are usually given in the form of cross sections as a function of kinetic energy. For the present table, these have been integrated over the Maxwell velocity distribution to obtain rate coefficients versus temperature, and in many cases the latter have been fit with an exponential, Arrhenius-type expression. As indicated in the reaction equation or by a footnote, such results do not correspond to an equilibrium distribution of the rotational, vibrational, and electronic levels of the reactants over the indicated temperature range, but usually to a room-temperature distribution.

In many acoustic and shock-tube experiments on vibrational excitation, only an overall relaxation time τ for the vibrational energy is measured, and not the actual populations of specific excited states. When the temperature is so low that the thermal mean energy, kT, is much less than the energy, hν, of the lowest excited vibrational level, the coefficient for excitation of this level may be readily determined from τ, since excitation of higher levels is negligible. At somewhat higher temperatures, where kT $\sim$ hν and higher levels cannot be completely ignored, it can be shown that the deexcitation coefficient for the lowest level is given by$^{(90,91)}$

$$\text{deexc. coeff. } (v = 1 \rightarrow 0) = \frac{kT}{p\tau(1-e^{-h\nu/kT})} ,$$

where p is the pressure. This result is based on a relation between excitation and deexcitation coefficients derived from detailed balance, and a relation between the $v = n \to n - 1$ and the $v = 1 \to 0$ coefficients from perturbation theory.

When $kT > h\nu$ the perturbation approach becomes inaccurate and transitions with $\Delta v > 1$ may become significant.(92) Accordingly, only relaxation data for temperatures $kT \lesssim h\nu$ have been converted to deexcitation coefficients for the table. Moreover, for simplicity the quantity $1 - \exp(-h\nu/kT)$ in the above equation has often been replaced by its mean value over the pertinent temperature range. As is conventional, the deexcitation coefficient rather than the excitation coefficient is tabulated, because of its simpler temperature dependence. The corresponding excitation coefficient may be obtained by multiplying by $\exp(-h\nu/kT)$.

The first column in the table indicates the reaction type, as defined in Appendix A. A prime (') after the type symbol indicates the reverse reaction type, while a Q indicates a quenching reaction with unidentified products. In the reaction equation (column 2), when the internal states of the reactants are not specified (or indicated by footnote) they are understood to correspond to equilibrium at the temperature given in column 4. When the state of a product is not indicated, however, the ground vibrational and electronic state is meant, except in the reactions marked Q, or in reactions involving a chemical change. In the latter case, the state of the newly-produced species is frequently unknown.

In the table, the method used for the rate-coefficient determination is indicated in column 5 by the following words or abbreviations:

α-bomb. - α-particle bombardment
Atm. - upper-atmosphere observations
Dis. aft. - discharge afterglow
Dischg. - discharge (continuous)
El. b. - electron beam
El. bomb. - electron bombardment (continuous)
El. bomb. aft. - electron bombardment afterglow

El. swarm - electron swarm
Flame
Flo. aft. - flowing afterglow
Fla. phot. - flash photolysis
Flow
Fluor. - fluorescence
Ion beam
Laser pu. - laser pumping
Laser sc. - laser beam scattering
Photolys. - photolysis (steady)
Sh. int. - shock interferometry
Sh. ioniz. - shock ionization
Sh. IR - shock infrared emission
Sh. Na - shock sodium-seeded emission
Sh. rad. - shock radiation
Sh. UV - shock ultraviolet absorption
Th. beam - thermal beam
Theor. - theoretical calculation
Ultras. - ultrasonic absorption

Table -- Rate Coefficients for Excitation, Deexcitation, and Excitation Transfer

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (^{o}K)	Type of Determ.	Footnotes & Refs.
1a	$e + H_2(v=0) \rightarrow e + H_2^{\dagger}(v=1)$	$(2.1\pm 0.7)x10^{-9}\ T^{0.1}\ e^{-12,590/T}$	1500-15,000	El. beam	a,b,18,93
1a	$e + CO(v=0) \rightarrow e + CO^{\dagger}(v=1\text{-}8)$	$(2.7^{+2.7}_{-1.4})x10^{-12} T\ e^{-4320/T}$	1500-10,000	El. beam	a,b,18
1a	$e + N_2(v=0) \rightarrow e + N_2^{\dagger}(v=1)$	$(1.0\pm 0.2)x10^{-9}\ e^{-14,900/T}$	2000-15,000	El.b., swarm	a,b,18,25
1b	$e + H(1^2S) \rightarrow e + H^*(2^2S)$	$(7 \pm 2)\ x10^{-7}\ T^{-0.5}\ e^{-121,700/T}$	3000-20,000	El. beam	a, 94
1b	$e + He(1^1S) \rightarrow e + He^*(2^3S)$	$(3.5\pm 1)\ x10^{-5}\ T^{-1}\ e^{-234,000/T}$	4000-20,000	El. beam	a, 95
1b	$e + Na(3^2S) \rightarrow e + Na^*(3^2P)$	$(6 \pm 2)\ x10^{-10}\ T^{0.6}\ e^{-24,540/T}$	1500-20,000	El. beam	a,96,97
1b	$e + K(4^2S) \rightarrow e + K^*(4^2P)$	$(1.4\pm 0.5)x10^{-8}\ T^{0.4}\ e^{-19,310/T}$	1500-20,000	El. beam	a,98
1b	$e + Rb(5^2S) \rightarrow e + Rb^*(5^2P)$	$(2.6\pm 0.9)x10^{-8}\ T^{0.3}\ e^{-18,390/T}$	1500-20,000	El. beam	a,98
1b	$e + Cs(6^2S) \rightarrow e + Cs^*(6^2P)$	$(2.2\pm 0.7)x10^{-8}\ T^{0.4}\ e^{-16,690/T}$	1500-20,000	El. beam	a,98,99
1b	$e + Cd(5^1S) \rightarrow e + Cd^*(6^3S)$	$2\ x10^{-11}$	15,000	Dischg.	34
1b	$e + Hg(6^1S) \rightarrow e + Hg^*(6^3P_o)$	$(4\pm 1)x10^{-2}\ T^{-1.5}\ e^{-64,600/T}$	6000-20,000	El.b.,Theor.	100
1b	$e + N_2(X^1\Sigma,v=0) \rightarrow e + N_2^*(A^3\Sigma)$	$(5\pm 2)x10^{-5}\ T^{-0.8}\ e^{-80,300/T}$	2000-20,000	El. swarm	a,b,25
1b	$e + N_2(X^1\Sigma,v=0) \rightarrow e + N_2^*(a^1\Pi)$	$(6\pm 2)x10^{-6}\ T^{-0.6}\ e^{-99,600/T}$	2000-20,000	El. swarm	a,b,25
1b'	$e + N^*(^2D) \rightarrow e + N(^4S)$	$(1.4\pm 0.6)x10^{-11}\ T^{0.6}$	400-20,000	Theor.	101
1b'	$e + O^*(^1D) \rightarrow e + O(^3P)$	$(2.7\pm 1.1)x10^{-11}\ T^{0.6}$	400-20,000	Theor.	101

Table -- Cont.

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (°K)	Type of Determ.	Footnotes & Refs.
1f	$e + O_2^+ \rightarrow O^* + O$	8×10^{-8} (tot. O^* ^1D) 4×10^{-8} (tot. O^* ^1S)	~ 300	Flo. aft.	36
2a'	$AB^\dagger(v=1) + X \rightarrow AB(v=0) + X$ $AB = CO, N_2, O_2, F_2, Cl_2, Br_2, I_2$; $X = AB, H_2, He, Ar$	$(1.4 \pm 0.7) \times 10^{-14} T \exp[0.00116 \mu^{1/2} \theta^{4/3} (0.015 \mu^{1/4} - T^{-1/3})]$ $\theta = h\nu/k$, μ = red. mass	~300-4000	Various	84
2a'	$H_2^\dagger(v=1) + H_2 \rightarrow H_2(v=0) + H_2$	$(4.3 \pm 0.4) \times 10^{-17}$ $(2.6 \pm 0.5) \times 10^{-13}\ T\ e^{-(100 \pm 3)/T^{1/3}}$	300 1100-2700	Laser sc. Sh. int.	102 103
2a'	$H_2^\dagger(v=1) + Ar \rightarrow H_2(v=0) + Ar$	$(1.1 \pm 0.3) \times 10^{-13}\ T\ e^{-(100 \pm 3)/T^{1/3}}$	1500-2700	Sh. int.	103
2a'	$CO^\dagger(v=1) + CO \rightarrow CO(v=0) + CO$	$(3 \pm 0.6) \times 10^{-12}\ T\ e^{-175/T^{1/3}}$	1200-4000	Sh. IR, Na, int.	84
2a'	$CO^\dagger(v=1) + Ar \rightarrow CO(v=0) + Ar$	$(1.2 \pm 0.2) \times 10^{-11}\ T\ e^{-213/T^{1/3}}$	1800-2500	Sh. IR	84
2a'	$N_2^\dagger(v=1) + N_2 \rightarrow N_2(v=0) + N_2$	$(1.3 \pm 0.2) \times 10^{-11}\ T\ e^{-220/T^{1/3}}$	1500-5000	Sh. IR, int.	84,104
2a'	$NO^\dagger(v=1) + NO \rightarrow NO(v=0) + NO$	$(6 \pm 1) \times 10^{-15}\ e^{T/1280}$	300-4000	Sh. UV, Fla. ph., Ultras.	105
2a'	$O_2^\dagger(v=1) + O_2 \rightarrow O_2(v=0) + O_2$	$(1.0 \pm 0.2) \times 10^{-12}\ T\ e^{-129/T^{1/3}}$	500-4000	Sh. UV, int.; Ultras.	84
2a'	$O_2^\dagger(v=1) + Ar \rightarrow O_2(v=0) + Ar$	$(3.5 \pm 0.6) \times 10^{-12}\ T\ e^{-165/T^{1/3}}$	900-3500	Sh. UV, int.	84
2a'	$F_2^\dagger(v=1) + F_2 \rightarrow F_2(v=0) + F_2$	$(1.1 \pm 0.2) \times 10^{-13}\ T\ e^{-65/T^{1/3}}$	300-400	Ultras.	84
2a'	$H_2O^\dagger(010) + H_2O \rightarrow H_2O(000) + H_2O$	$(7 \pm 2) \times 10^{-12}$	323	Ultras.	106
2a'	$CO_2^\dagger(010) + CO_2 \rightarrow CO_2(000) + CO_2$	$\sim 2 \times 10^{-10}\ e^{-77/T^{1/3}}$	300-1200	Sh. int., Ultras.	107,108

Table -- Cont.

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (°K)	Type of Determ.	Footnotes & Refs.
2b	$CO^{\dagger}(v=1) + NO \rightarrow CO + NO^{\dagger}(v=1)$	$(1.4\pm0.7)\times10^{-12}\ T^{\frac{1}{2}}\ e^{-48/T^{1/3}}$	300-2200	Sh.IR,Fl.ph.	109
2b	$N_2^{\dagger}(v=1) + NO \rightarrow N_2 + NO^{\dagger}(v=1)$	$(1.6\pm0.8)\times10^{-12}\ T^{\frac{1}{2}}\ e^{-69/T^{1/3}}$	300-3300	Sh.IR,Fl.ph.	109
2b	$N_2^{\dagger}(v=1) + O_2 \rightarrow N_2 + O_2^{\dagger}(v=1)$	$(3.6\pm1.8)\times10^{-12}\ T^{\frac{1}{2}}\ e^{-110/T^{1/3}}$	800-2600	Sh.IR,int.	104,109
2b	$NO^{\dagger}(v=1) + H_2O \rightarrow NO + H_2O^{\dagger}(010)$	$(1.5\pm0.2)\times10^{-12}$	~ 300	Fla.phot.	111
2b	$CH_4^{\dagger}(v_3=1) + CH_4 \rightarrow CH_4^{\dagger\dagger}(v_4=1,2) + CH_4$	$(7\pm2)\times10^{-12}$	~ 300	Fluor.	110
2b	$CO_2^{\dagger}(001) + N_2 \rightarrow CO_2 + N_2^{\dagger}(v=1)$	$(1.9\pm0.6)\times10^{-16}\ T^{\frac{1}{2}}$	750-2000	Sh.IR	109
2c	$Ar(^1S) + Ar \rightarrow Ar^*(4s) + Ar$	$(2.3\pm0.3)\times10^{-15}\ T^{\frac{1}{2}}\ e^{-134,000/T}$	5000-9000	Sh.ioniz.	47
		$(5\pm2)\times10^{-21}\ T^2\ e^{-134,000/T}$	15,000-20,000	Sh.ioniz.	48
2c	$Kr(^1S) + Kr \rightarrow Kr^*(5s) + Kr$	$(1.6\pm0.2)\times10^{-15}\ T^{\frac{1}{2}}\ e^{-115,000/T}$	5000-9000	Sh.ioniz.	47
2c	$Xe(^1S) + Xe \rightarrow Xe^*(6s) + Xe$	$(1.3\pm0.2)\times10^{-16}\ T^{\frac{1}{2}}\ e^{-96,500/T}$	5000-9000	Sh.ioniz.	47
2c	$Xe(^1S) + Ar \rightarrow Xe^*(6s) + Ar$	$(3.9\pm0.8)\times10^{-16}\ T^{\frac{1}{2}}\ e^{-96,500/T}$	5000-9000	Sh.ioniz.	47
2c	$N_2(X^1\Sigma) + N \rightarrow N_2^*(A^3\Sigma) + N$	$(1.9\pm0.8)\times10^{-6}\ T^{-3/2}\ e^{-71,600/T}$	7000-19,000	Sh.rad.	46
2c'	$O^*(^1D) + O \rightarrow O(^3P) + O$	$< 4 \times 10^{-13}$	~ 300	Dischg.	55
	$+ He \rightarrow O(^3P) + He$	1.5×10^{-15}	~ 300	Flo.aft.	112
2c'	$Ne^{**}(^3P_1) + Ne \rightarrow Ne^*(^3P_2) + Ne$	$(4.6\pm0.7)\times10^{-15}\ e^{0.0078T}$	200-500	Dis.aft.	33
2c'	$Na^{**}(3^2P_{3/2}) + M \rightarrow Na^*(3^2P_{\frac{1}{2}}) + M$	$(7.0\pm0.4)\times10^{-10}$ (M=He) $(4.2\pm0.2)\times10^{-10}$ (M=Ar)	397	Fluor.	113

Table -- Cont.

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (°K)	Type of Determ.	Footnotes & Refs.
2c'	$K^{**}(4^2P_{3/2}) + M \rightarrow K^*(4^2P_{1/2}) + M$	$(6.0\pm0.3)\times10^{-10}$ (M=He)	368	Fluor.	114
		$(1.4\pm0.1)\times10^{-10}$ (M=Ar)	368		
		$(1.6\pm0.5)\times10^{-9}$ (M=K)	368		
2c'	$Rb^{**}(5^2P_{3/2}) + Rb \rightarrow Rb^*(5^2P_{1/2}) + Rb$	$(2.9\pm0.4)\times10^{-10}$	360	Fluor.	115
		$(3.1\pm0.5)\times10^{-10}$	380		
2c'	$Cs^*(6^2P_{3/2}) + M \rightarrow Cs^*(6^2P_{1/2}) + M$	$(5.4\pm0.5)\times10^{-15}$ (M=He)	350	Fluor.	116
		$(2.6\pm0.3)\times10^{-15}$ (M=Ar)	350	Fluor.	116
		$(1.0\pm0.1)\times10^{-10}$ (M=Cs)	350	Fluor.	117
		$(5.4\pm0.5)\times10^{-10}$ (M=H_2)	312	Fluor.	118
		$(8.7\pm0.9)\times10^{-11}$ (M=N_2)	312	Fluor.	118
2c'	$NO^*(X^2\Pi_{3/2}) + NO \rightarrow NO(X^2\Pi_{1/2}) + NO$	$(2.6\pm0.3)\times10^{-12}$	296	Ultras.	119
2d	$N_2^\dagger(v \gtrsim 7) + Na \rightarrow N_2 + Na^*(3^2P)$	$\sim 10^{-10}$	2100-2800	Th.beam	52
2d	$2OH^\dagger(v \gtrsim 5) \rightarrow OH^*(A^2\Sigma) + OH$	$\sim 10^{-10}$	~ 3500	Flame	120
2d'	$Hg^*(6^3P_1) + CO \rightarrow Hg + CO^\dagger(v)$	$(4^{+5}_{-2})\times10^{-12}$ (v=2)	~ 350	Fluor.	49
		$(5^{+7}_{-3})\times10^{-14}$ (v=9)			
		$< 3\times10^{-14}$ ($v\geq10$)			
2d'	$Hg^*(6^3P_1) + NO \rightarrow Hg + NO^\dagger(v)$	$(1.0^{+2.0}_{-0.8})\times10^{-11}$ (v=2)	~ 300	Fluor.	50
		$(5^{+11}_{-4})\times10^{-13}$ (v=16)			
		$< 2\times10^{-13}$ ($v\geq18$)			
2e	$He^{**}(n^1P) + He \rightarrow He^*(n^1F) + He$	$(2.4\pm0.6)\times10^{-9}$ (n=4)	~ 300	El.bomb.aft.	58
		$(3\pm1)\times10^{-9}$ (n=5)			
	$\rightarrow He^*(n^3F) + He$	$(1.2\pm0.6)\times10^{-9}$ (n=4)			
		$(8\pm2)\times10^{-9}$ (n=5)			

Table -- (Cont.)

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (^oK)	Type of Determ.	Footnotes & Refs.
2e	$He^*(2^3S) + Ne \rightarrow He + Ne^*(2s_3)$ $\rightarrow He + Ne^*(2s_2)$	$(2.2\pm0.6)\times10^{-12}$ $(3.9\pm1.2)\times10^{-12}$	400	Laser pu.	121
2e	$O^*(^1D) + O_2 \rightarrow O(^3P) + O_2^*(b^1\Sigma)$	$\gtrsim 10^{-11}$	~ 300	Flo.aft.	122
2e	$Ar^*(4^3P_2) + N_2 \rightarrow Ar + N_2^*(C^3\Pi)$	$(3\pm1)\times10^{-11}$	300	α-bomb.	123
2e	$Hg^*(6^3P_1) + Zn \rightarrow Hg + Zn^*(4^3P_1)$	5×10^{-14}	736	Fluor.	124
2e	$Hg^*(6^3P_1) + Tl \rightarrow Hg + Tl^*(7^2S)$	$(7\pm2)\times10^{-10}$	933,1073	Fluor.	125
2e	$2\ O_2^*(a^1\Delta) \rightarrow O_2^{**}(b^1\Sigma) + O_2$	2×10^{-18}	~ 300	Flo.aft.	126
2e	$N_2^*(?) + NO \rightarrow N_2 + NO^*(A^2\Sigma)$	$\sim 3\times10^{-12}$	~ 300	Th.beam	127
2f	$He^*(2^3S) + M \rightarrow He + M^+ + e$	$(9\pm2)\times10^{-11}$ (M=Ar) $(1.3\pm0.3)\times10^{-10}$ (M=Kr) $(1.8\pm0.4)\times10^{-10}$ (M=Xe) $(1.0\pm0.4)\times10^{-10}$ ($M=N_2$)	~ 300	Dis.aft., flo.aft.	128,129
2f	$2\ He^*(2^3S) \rightarrow He + He^+ + e$	$(2.8\pm0.7)\times10^{-9}$	520	Dischg.	130
2f	$He^*(60\%\ 2^1S + 40\%\ 2^3S) + O_2$ $\rightarrow He + O_2^+ + e$	$(1.3\pm0.3)\times10^{-10}$	~ 300	Th.beam	131
2f	$O_2^*(a^1\Delta) + O_2^- \rightarrow 2\ O_2 + e$	$10^{-9\pm1}$	~ 300	Dis.aft.	132
2g	$He^*(3^3D) + He \rightarrow He_2^+ + e$	2.9×10^{-10}	400	Dischg.	133
2g	$2Cs^*(6p) \rightarrow Cs_2^+ + e$	$(3\pm2)\times10^{-13}$	500	Fluor.	134
2h'	$O^{+*}(^2D) + N_2(v=0) \rightarrow O + N_2^+$	$\sim 10^{-9}$	20,000	Ion beam	a,b,135

Table -- Cont.

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (°K)	Type of Determ.	Footnotes & Refs.
2j	$N + NO \rightarrow N_2^\dagger (v_{mean}=3) + O$	$(2.2\pm0.6)\times10^{-11}$	300	Flo.aft.	136,137
2j	$Na + KBr^\dagger(v_{mean}\sim 70) \rightarrow K^*(4p)+NaBr$	$\sim 10^{-9}$	~ 700	Th. beam	138
2j	$K + Br_2 \rightarrow KBr^\dagger(v_{mean}\sim 70) + Br$	1.3×10^{-9}	~ 600	Th. beam	22,139
2j	$C_2 + OH \rightarrow CH^*(A^2\Delta) + CO$	$\sim 10^{-12}-10^{-11}$	~2500	Flame	140
2j	$NO + O_3 \rightarrow NO_2^* + O_2$	$\sim 10^{-12}\, e^{-(2090\pm150)/T}$	216-322	Flow	141
2j'	$O^*(^1D) + O_3 \rightarrow O_2 + O_2$	$4\times10^{-10}\, e^{-(1200\pm500)/T}$	273-323	Flo.aft.	112
2j'	$Ne^*(3s\,^3P_2) + H_2 \rightarrow Ne + H^*(n=3)+H$	6×10^{-11}	~ 600	Dischg.	142
2j'	$N_2^\dagger(v=3) + O^+ \rightarrow NO^+ + N$	$\sim 1\times10^{-10}$	~ 300	Flo.aft.	66
2j'	$N_2^\dagger(v\geq4) + O_3 \rightarrow N_2 + O_2 + O$	$(5.4\pm1.1)\times10^{-13}$	~ 300	Flo.aft.	143
2j'	$N_2^*(B^3\Pi) + CO_2 \rightarrow N_2 + CO + O$	$(8.5\pm1.3)\times10^{-11}$	196	Flo.aft.	144
2j'	$N_2^*(B^3\Pi) + N_2O \rightarrow N_2 + N_2 + O$ or $N_2 + N + NO$	$(5.8\pm0.7)\times10^{-11}$	195	Flo.aft.	144
2j'	$N_2^{+*}(^4\Sigma) + N_2 \rightarrow N_3^+ + N$	$(6\pm1)\times10^{-11}$ 6×10^{-10}	~ 300 ~ 300	El.bomb.aft. El.bomb.	145 146
2j'	$NO^*(A^2\Sigma) + NO \rightarrow N_2 + O_2$ $\rightarrow N_2O + O$	$\sim 1.7\times10^{-10}$ $\sim 7\times10^{-11}$	~ 300 ~ 300	Photolys. Photolys.	147 148
2j'	$O_2^*(^1\Sigma + {}^1\Delta) + CO \rightarrow CO_2 + O$	$\sim 10^{-25}$	353		149
2j'	$O_2^*(^1\Sigma + {}^1\Delta) + O_3 \rightarrow 2\ O_2 + O$	1.7×10^{-14}	~ 300	Flo.aft.	150

Table -- (Cont.)

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature (^oK)	Type of Determ.	Footnotes & Refs.
2Q	$N^*(^2D) + O_2 \rightarrow N + O_2$ or $NO + O$	$\sim 10^{-12}$	~ 300	Atm.	55,151
2Q	$O^*(^1S) + O \rightarrow 2\ O$ or $O^*(^1D)$	1.8×10^{-13}	~ 300	Flo.aft.	152,153
	$+ O_2 \rightarrow O$ or $O^* + O_2$	1.0×10^{-13}	~ 300	Flo.aft.	153
2Q	$Na^*(3^2P) + H_2 \rightarrow Na + H_2$ or $H_2^\dagger$	$(3.0\pm0.1)\times10^{-10}$	~ 300	Fluor.	154
		$(4.0\pm0.1)\times10^{-10}$	1600-1800	Flame	155
2Q	$Na^*(3^2P) + N_2 \rightarrow Na + N_2$ or $N_2^\dagger$	$(2.2\pm0.1)\times10^{-10}$	~ 300	Fluor.	154
		$(3.6\pm0.1)\times10^{-10}$	1400-1800	Flame	155
2Q	$I^*(5^2P_{\frac{1}{2}}) + M \rightarrow I(5^2P_{3/2}) + M$	2.1×10^{-16} ($M=N_2$)	~ 300	Fla.phot.	156
		1.1×10^{-11} ($M=NO$)			
		5×10^{-12} ($M=O_2$)			
2Q	$N_2^*(A^3\Sigma) + M \rightarrow N_2$ or $N_2^\dagger + M$	5×10^{-11} ($M=N$)	~ 300	Flo.aft.	157
		$\leq 3\times10^{-11}$ ($M=O$)	~ 300	Atm.	55
		7×10^{-11} ($M=NO$)	~ 300	Flo.aft.	157
		$\leq 4\times10^{-10}$ ($M=O_2$)	~ 300	Atm.	55
2Q	$N_2^*(B^3\Pi, v=0) + NO \rightarrow N_2 + NO$	4×10^{-15}	~ 300	Dis.aft.	158
2Q	$N_2^*(C^3\Pi, v=0) + M \rightarrow N_2 + M$	$(9\pm3)\times10^{-12}$ ($M=N_2$)	~ 300	El.bomb.	54,159
		$(2.5\pm0.7)\times10^{-10}$ ($M=O_2$)	~ 300	El.bomb.	159
2Q	$N_2^{+*}(A^2\Pi, v=2) + N_2 \rightarrow N_2^+ + N_2$	1×10^{-9}	~ 300	El.bomb.	160
2Q	$N_2^{+*}(B^2\Sigma, v=0) + M \rightarrow N_2^+ + M$	$(4.4\pm0.7)\times10^{-10}$ ($M=N_2$)	~ 300	El.bomb.	54,159
		$(8.0\pm1.4)\times10^{-10}$ ($M=O_2$)	~ 300	El.bomb.	159
2Q	$NO^*(A^2\Sigma) + M \rightarrow NO + M$	8×10^{-14} ($M=He$)	400	Fluor.	161
		2×10^{-13} ($M=H_2$)			
		7×10^{-13} ($M=N_2$)			
		4×10^{-10} ($M=NO$)			

Table -- Cont.

Reaction Type	Reaction	Rate Coefficient (cm^3/sec)	Temperature ($^\circ K$)	Type of Determ.	Footnotes & Refs.
2Q	$O_2^*(a^1\Delta) + O \rightarrow O_2 + O$	2×10^{-14}	~ 300	Atm.	55
2Q	$OH^*(A^2\Sigma, v=0) + M \rightarrow OH + M$	$(1.3 \pm 0.2) \times 10^{-10}$ ($M=N_2$) $(1.8 \pm 0.4) \times 10^{-10}$ ($M=O_2$) $(7 \pm 1) \times 10^{-10}$ ($M=H_2O$)	1500-1800	Flame	162
	Three-body Reaction	(cm^6/sec)			
4a	$He^*(^3S) + 2\ He \rightarrow He_2^*(^3\Sigma) + He$	$3.6 \times 10^{-33}\ e^{-780/T}$	280-370	Dis.aft.	163
4a	$N + N + M \rightarrow N_2(B^3\Pi) + M$	3.8×10^{-33} ($M=He$) 4×10^{-33} ($M=Ar$) 1.7×10^{-34} ($M=N_2$)	~ 300 ~ 300 ~ 300	Flo.aft. Flo.aft. Flo.aft.	69 69 69,164
4a	$N + O + N_2 \rightarrow NO^*(B^2\Pi) + N_2$	1×10^{-34}	~ 300	Flo.aft.	69
4a	$O + O + M \rightarrow O_2^*(b^1\Sigma) + M$	1.3×10^{-36} ($M=He$) 3.3×10^{-37} ($M=Ar$) 1.7×10^{-37} ($M=N_2$)	~ 300	Flo.aft.	69
4a	$O + O + N_2 \rightarrow O_2^*(A^3\Sigma) + N_2$	2.1×10^{-37}	~ 300	Flo.aft.	69
4a	$H + H_2 + O_2 \rightarrow OH^*(A^2\Sigma) + H_2O$	5×10^{-37}	1000-1900	Sh.rad.	165
4a'	$O^*(^1D) + 2\ O_2 \rightarrow O_3 + O_2$	2×10^{-34}	~ 300	Flo.aft.	112
4b	$H + H + Na \rightarrow H_2 + Na^*(^2P)$	5×10^{-31}	1250-1500	Flame	73
4b	$N + O + O \rightarrow NO + O^*(^1S)$	3×10^{-33}	~ 300	Flo.aft.	69
4b	$O + O + O \rightarrow O_2 + O^*(^1S)$	1.5×10^{-34}	~ 300	Flo.aft.	69

Table -- Cont.

Reaction Type	Three-body Reaction	Rate Coefficient (cm^6/sec)	Temperature (^oK)	Type of Determ.	Footnotes & Refs.
4b	$0 + 0 + Na \rightarrow 0_2 + Na^*(^2P)$	$1.5x10^{-29}$	1250-1500	Flame	73
4b	$0 + 0 + CN \rightarrow 0_2 + CN^*(A^2\Pi)$	10^{-31}-10^{-30}	~ 300	Fla.phot.	166
4b	$H + OH + K \rightarrow H_20 + K^*(^2P)$	$1.5x10^{-30}$	~ 2000	Flame	72
4b	$H + OH + OH \rightarrow H_20 + OH^*(A^2\Sigma)$	$2x10^{-32}$	~ 2000	Flame	72

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[a] This rate coefficient has been obtained by integrating the published cross section over a Maxwell velocity distribution for several temperatures, and fitting by an Arrhenius-type function of temperature. The indicated temperature limits correspond to the region of good fit; the region where the basic data are valid is generally broader.

[b] This rate coefficient applies to molecules having a rotational temperature of approximately 300°K (usual beam target-gas temperature). The value when the rotational temperature equals the electron temperature (column 4) differs by an unknown but probably not large factor in most cases.

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10. ABSTRACT

~~This~~ review summarizes present knowledge of the atomic and molecular mechanisms that produce or remove rotationally, vibrationally, and electronically excited species in heated or excited gases. A logical classification scheme for these mechanisms is introduced, and the extent of present information on each class is indicated. The validity and utility of several general rules and regularities are also examined. An appendix includes a table of rate coefficients for vibrational and electronic excitation and de-excitation reactions, taken directly from or derived from data in the literature. This table provides comprehensive coverage of some classes of reactions and representative coverage of the others.

11. KEY WORDS

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